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THE REFRACTIVE INDEX AND DENSITY OF POLYSTYRENE AND POLYVINYL TOLUENE LATICES

by

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Research on the Size and Shape of Large
Molecules and Colloidal Particles

Technical Report No. 7

THE REFRACTIVE INDEX AND DENSITY
OF SYNTHETIC LATICES

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Introductory Remarks

This report is a reproduction, without any changes, of the principal part of the master's thesis as written and submitted to Wayne University by Mr. Thomas L. Pugh.

In order to compare experimentally determined specific turbidities with the theoretical specific turbidities--as given in several preceding reports--it was necessary to know as accurately as possible, both the density and the refractive index of the light scattering particles in the polystyrene and polyvinyl toluene latices used as model systems by Mr. Richard Tabibian. The determination of these quantities is the subject of the work related in the following. Prior to publication of this material, it will be necessary to condense the material extensively.

Wilfried Heller

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THE REFRACTIVE INDEX AND DENSITY OF SYNTHETIC LATICES

CHAPTER I

INTRODUCTION

The density and refractive index of suspended particles are needed in investigations involving light scattering. These properties are also of an interest, in themselves. In this investigation it was necessary to find the ratio of the refractive indices of suspended particles to water. This quantity is used in the light scattering equation developed by Mie.[1]

The latices used in light scattering by Tabibian are those of polystyrene and polyvinyl toluene.[2] Since in light scattering a range of particle sizes are used it was decided that this investigation should also cover the same range of particle sizes.

Since a relatively more accurate result can be obtained with less effort by using differential techniques for refractive indices and densities, intereferometric and differential pycnometric methods were used for the determination of

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[1]G. Mie, <u>Ann</u>. <u>Physik</u>., 25, 377 (1908).

[2]R. Tabibian, Thesis, Wayne Univ. 1954, p. 2.

the respective properties. The advantage of both of these methods is that rigid temperature control is not necessary for accurate results. A second advantage in the differential pycnometric technique for density determinations is that most of the buoyancy corrections and weight calibrations need not be considered.

CHAPTER II

DENSITIES

A. The Literature Survey

Recently a few papers have been published which are similar to one phase of this investigation. In the determination of particle size with the ultracentrifuge a material is desirable for a check on the procedure. Some investigators have been using the well known Dow 580 G polystyrene latex. Kahler and Lloyd using a constant density gradient at 500 rps in D_2O and sucrose with 1% NaCl found the density of the suspended polystyrene particles to be 1.055 ± .001.[1] They found that particle density did not vary with the change in solvent (D_2O and sucrose) thus indicating that the polystyrene particle was completely hydrophobic and did not absorb any of the solvent.

Other investigators also using the ultracentrifuge reported a value for the density of polystyrene as 1.053 which was later revised to 1.054.[2,3] Still other investi-

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[1]H. Kahler and B. J. Lloyd, Jr., Science, 114, 34-35 (1951).

[2]D. G. Sharp and J. W. Beard, J. Biol. Chem., 185, 247 (1950).

[3]D. G. Sharp, J. Applied Phys., 21, 71 (1950).

gators determined the density of polystyrene on the dried material and reported a value of 1.052.[1]

Other values on the solid material are reported in a book by Boyer and Boundy.[2] They gave values of the density as 1.050, 1.030 and 1.022 for polystyrene, poly meta vinyl tolune, and poly para vinyl toluene, respectively.

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[1] R. C. Williams and R. C. Backus, J. Am. Chem. Soc., 71, 536 (1949).

[2] R. H. Boundy and R. F. Boyer, "Styrene," New York: Reinhold Publishers Corp., 1952, p. 1239.

B. Theoretical

The densities of the synthetic latices and of the particles themselves are necessary for the refractive index calculations. If one determines the particle density, by the use of a mixture equation, he may by the same token use the mixture equation to determine the density of a latex of any concentration.

Having decided to use a differential technique, a pair of differential pycnometers were made incorporating capillaries that had previously been calibrated. The need for the differential technique here was due to the fact that the densities of the two components of the system were so close: 0.997 for water and 1.05 for polystyrene. Therefore, high concentrations and good accuracy with as many significant figures as possible were needed for the latex density.

A pair of differential pycnometers must be as closely matched in volume and weight as possible. Both pycnometers must go through the same procedure when volume and weight measurements are made. One pycnometer contains the solvent and the other contains a solution, or in this investigation a latex sample. The quantity $\Delta d/\Delta t$ which is the density change with temperature change is small for solids but the range must be carefully controlled. The temperature range in this investigation never exceeded $\pm$ .003°C. Another thing that had to be carefully watched was temperature difference between the two samples. The procedure will be enlarged upon in the experimental section.

The phenomenon which allows one to use a simple equation for the differential density technique is the volume additivity of the particles and the water. As mentioned earlier, Kahler and Lloyd showed that the particles are completely hydrophobic. When one has volume additivity it is only necessary to determine the difference in density in the contents of the two pycnometers which was designated Δd.

(1) $$W_{12}-W_1 = d_{12}V_{12}-d_1V_1$$

(2) $$\text{but } d_{12} = d_1 + \Delta d$$

(3) $$\therefore W_{12}-W_1 = d_1V_{12} + \Delta d\, V_{12} - d_1V_1$$

rearranging: $$\Delta d = \frac{(W_{12}-W_1)-d_1(V_{12}-V_1)}{V_{12}}$$

where d_{12} = density of latex

d_1 = density of solvent

W_{12} = weight of latex

W_1 = weight of solvent

V_{12} = volume of latex

V_1 = volume of solvent

But Δd is never determined this simply; therefore one has to check on the importance of the buoyancy corrections, vapor corrections and weight calibrations. Since every pair of pycnometers is different, these quantities should all be checked by simulating two extreme sets of conditions. This was done in this investigation in the following manner:

1. Extremes in air density were set up.

2. Buoyancy corrections were calculated for the pycnometers when empty and full and placed in an equation similar to (3) only it included the pycnometer weights.

3. The difference in the air density above the liquid and outside the pycnometer was checked.

In this investigation the pycnometers differed in weight by 0.2 g. and in volume by 0.4 cc. All the buoyancy factors canceled out except for the difference in the volumes of the liquids. By putting the latex in the lighter but larger volume pycnometer one set of buoyancy corrections canceled out.

When one used the same weights in weighing the two pycnometers, some of their weight corrections canceled. For example, if one pycnometer, when full, always weighed 42 g. and the other always 41 g., this meant that only the weight calibrations of the 2 g., 1 g., and fractional weights had to be used because the weight calibrations for the other 40 g. would cancel out. Even the meniscus corrections cancel out whether the upper or lower part of the meniscus was measured as long as both pycnometers were done in the same way. This is only true when both capillaries have approximately the same diameter. The final equation used in this investigation was:

(4) $$\Delta d = \frac{(W'_{12} - W'_1) - (P_{12} - P_1) - d_1(V_{12} - V_1) + D_{air}(V_{12} - V_1)}{V_{12}}$$

where P_{12} and P_1 = empty pycnometer weights

W'_{12} and W'_1 = full pycnometer weights

D_{air} = density of air.

Once Δd was obtained it was added to the solvent density to give:

(5) $$d_1 + \Delta d = d_{12}$$

The equation used to obtain densities of suspended particles yields apparent densities but in the case of volume additivity and perfect hydrophobic nature of the polystyrene and polyvinyltoluene particles, the apparent and the true density are identical.[1]

(6) $$\frac{1}{d_{12}} = \frac{c_1}{d_1} + \frac{c_2}{d_2},$$

which, however, is normally found using the respective specific volumes:

(7) $$\theta_{12} = c_1\theta_1 + c_2\theta_2$$

where θ_{12} = specific volume of latex

θ_1 = specific volume of solvent

θ_2 = specific volume of particle

c_2 = weight fraction of particle

c_1 = weight fraction of solvent.

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[1] W. Heller and A. Thompson, J. Colloid Sci., 6, 58 (1951).

It was found, however, that the latices contained water-soluble material of high density which was assumed in the first approximation to be volume additive. This was the only way in which the effect on the density of the particle could be evaluated. The ratio of the H_2O-soluble material to the polymer (K) had to be determined as well as its apparent density by using the serum. Thus in the final evaluation of d_2, a variation of equation (6) was used. First it was extended to include three components and then the ratio, K, was used in an expression with the weight fractions of the dried polymer and the water-soluble materials.

(7a) $$\frac{W_3}{W_2} = K = \text{ratio}$$

where W_3 and W_2 = weights of water-soluble material and polymer, respectively, in the latex sample.

(8) $$\frac{\frac{W_3}{W_{123}}}{\frac{W_2}{W_{123}}} = K = \frac{c_3}{c_2} \qquad W_{123} = \text{weight of latex.}$$

This ratio is a constant even after evaporation or dilution of the latex.

(9) $$c_1 + c_2 + c_3 = 1$$

and substituting (8) into (9)

(10) $$c_1 + c_2 + c_2K = 1$$

(11) $$c_2 = \frac{1-c_1}{1+K}$$

The equation for density with three components is:

(12) $$\theta_{123} = \theta_1 c_1 + \theta_2 c_2 + \theta_3 c_3$$

where c_3 and θ_3 = weight fraction and specific volume, respectively, for the water-soluble component.

Substituting for c_2 and c_3:

(13) $$\therefore \theta_{123} = \theta_1 c_1 + \frac{(1-c_1)\theta_2}{(1 + K)} + \frac{(1-c_1)K\theta_3}{(1 + K)}$$

and on solving for θ_2:

(14) $$\theta_2 = \frac{1}{d_2} = \frac{\left[\theta_{123} - \theta_1 c_1 - \frac{(1-c_1)\theta_3 K}{1 + K}\right] (1 + K_1)}{1 - c_1}$$

(15) $$\theta_2 = \frac{1}{d_2} = \frac{\theta_{123}(1 + K) - \theta_1 c_1 (1 + K)}{1-c_1} - \theta_3 K$$

C. Experimental

The measurement of the densities required a great deal of preparation. This section will deal with the calibration of the capillaries and the pycnometers, themselves. Also in this section, the use of the pycnometers and a sample procedure will be explained.

1. Capillary Calibration

Besides using the conveniency of differential pycnometers, it was decided to also incorporate calibrated capillaries. This allows one to fill the pycnometer with little regard to the position of the meniscus except that it lie within a 2-3 cm. range of a mark on the stem of the pycnometer which contains the capillary. Knowing the radius of capillary, the volume of the pycnometer to the mark, and the distance of the meniscus from the mark, the volume of liquid can be calculated, no matter where the meniscus.

There are two approaches to the determination of the radius of a capillary. The most convenient type of radius measurement is made on a piece of constant bore capillary, however, this type of capillary is the most difficult type to obtain. Since two pieces of capillary were needed, about 8 cm. in length, it would be twice as difficult to locate two good pieces of constant bore capillary. The alternate method is to just take two pieces of capillary of relatively constant bore and measure their radii the entire length of the capillary. Using this plan, the variation in the volume was plotted against l. l is the distance from the mark on the glass stem to the meniscus. Thus if the volume of a liquid in the pycnometer is needed, the volume above or below the mark in the capillary may be selected from the plot corresponding to the measured l and added or substracted to the volume of the pycnometer at the mark.

The physcial capacity of a pycnometer and the radius of the capillary were determined by the needs of d_2. Four significant figures were wanted for the d_2. The maximum capillary radius allowed to take advantage of the precision obtainable in the overall procedure can be determined. The W measurements can be made to 0.01 mg. with a total weight of 20 g. The Δl, or the distance of the meniscus from the scratch line of known volume, was determined by a traveling microscope which was capable of reproducing lengths to $\pm 5 \times 10^{-4}$. The total volume of the pycnometer was 20 cc. Thus, these measurements would yield up to seven significant figures for $\Delta d/d$.

However, the concentration can only be determined to five significant figures on using the drying procedure mentioned above. Therefore the value of d_{12} in the following equation should also be known to five figures. Since d_1 is known to six significant figures, this means that Δd has to be known to an accuracy of at least 1×10^{-6}.

From II (6):

$$\frac{1}{d_{12}} = \frac{c_1}{d_1} \quad \frac{c_2}{d_2}$$

(1)

$$d_2 = \frac{c_2 d_1 d_{12}}{d_1 - c_1 d_{12}}$$

In order to determine the maximum capillary diameter necessary to yield a precision of 1×10^{-6} an ideal experiment was postulated where the two pycnometers were filled with exactly the same weight of material. Therefore:

$$d_1 = \frac{W_1}{V_1}, \qquad d_2 = \frac{W_1}{V_2}$$

where: W_1 = weight of pycnometer contents

V_1 and V_2 = volumes of the respective pycnometers

$\triangle V$ = minimum measurable volume

$\triangle d$ = minimum detectable density

$\triangle 1$ = minimum measurement of capillary height.

By subtraction: $d_1 - d_2 = \frac{W_1}{V_1} - \frac{W_1}{V_2}$

$$\triangle d = W_1 \left(\frac{V_2 - V_1}{V_1 V_2} \right)$$

$$\triangle d = \frac{-W_1 \triangle V}{V_1 V_2}$$

$$\triangle d = \frac{-W_1 \triangle V}{V_1 (V_1 + \triangle V)}$$

$$\triangle V = \frac{-V_1^2 \triangle d}{V_1 \triangle d + W_1} = \pi r^2 \triangle 1$$

$$r^2 = \frac{-V_1^2 \triangle d}{\pi \triangle 1 \ (V \triangle d + W_1)}$$

$$r^2 = \frac{400 \times 10^{-6}}{\pi \times 5 \times 10^{-4} (20 \times 10^{-6} + 20)}$$

$$r^2 = 1.27 \times 10^{-2}$$

$$r = 1.13 \times 10^{-1} = .113 \text{ cm.}$$

$$= 1.1 \text{ mm.}$$

$$\text{diameter} = 2.3 \text{ mm.}$$

The largest capillary used in making the pycnometers was only 1.2 mm. in diameter. For this reason they can be used for even more accurate work than intended in this experiment.

A further restriction in the determination of d_2 was found in equation (1). The denominator in that expression must have five significant figures, therefore a minimum value of c_1 will be required, on the supposition that Δc is $\pm$ .00001 g./g.

Assuming: $d_{12} \cong 1.00$, and inserting values into: $d_1 - c_1 d_{12} = .10000$, the final result is: $.99705 - c_1 - .10000$

$$c_1 \ll .89705$$

and consequently the approximate minimum concentration of latex:

$$c_2 \gg .10 \text{ g./g. or } 10\%.$$

For the actual calibration of the capillaries, the glass was first carefully scratched about midway from each end for reference mark. The two capillaries were then labeled by scratching identifying marks on them. They were referred to as capillary number one and number two. The ends also had to be marked to identify one end from another. The ends were called + and -.

The technique in measuring the length of a volume mercury from one end of a capillary to the other is quite unique and was suggested by Thompson.[1] It eliminated the troublesome meniscus correction.

The principle is illustrated by imagining two superimposed volumes of mercury one long and the other short. See Figure 12 a. L_2 equals the length of the longer volume of mercury and L_1 the shorter length.

In Figure 12 b the ideal case is considered where two of the ends coincide. Thus if L_1 is subtracted from L_2 the volume in the shaded area is obtained. One of the ends of the volume of mercury is concave and the other convex. If the capillary bore is relatively uniform, the volume in the shaded projection is exactly equal to that volume cut out of the shaded area by L_1. Therefore one can see that L_3 corresponds to a perfect cylinder of mercury and needs no meniscus corrections.

Using this technique as a basis for the calibration, a modification was developed whereby a small length of the capillary was determined absolutely by the exact method mentioned above. Once this had been established larger volume of mercury was run through the capillary in overlapping steps. The following equations were used to determine the radii of capillaries. See Figure 13 for illustration.

Using Figure 13 a where a small volume of mercury, V_I, is superimposed over a large volume, V_{III}, the radius in the

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[1] A. Thompson, Thesis, Wayne Univ., 1949, p. 54.

FIG. 12

BASIC IDEA OF MENISCUS CORRECTION IN CAPILLARY CALIBRATION

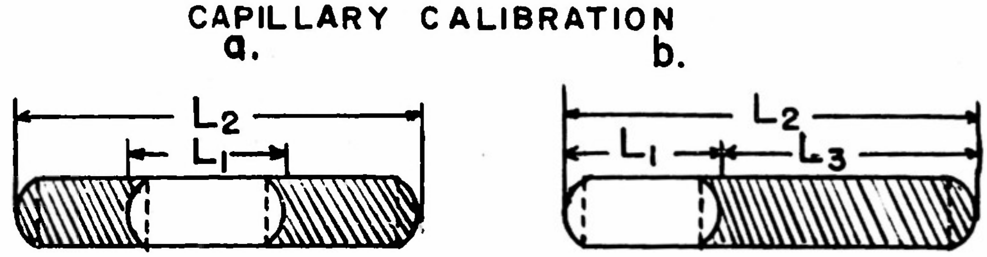
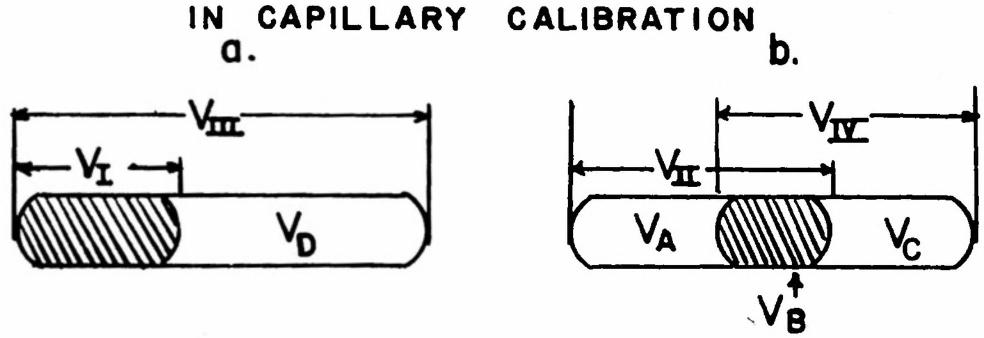


FIG. 13

PRACTICAL APPLICATION OF MENISCUS CORRECTION IN CAPILLARY CALIBRATION



unshaded area is determined:

(2) $$V_D = V_{III} - V_I$$

V's = volumes of mercury

(3) $$\pi r^2 l_D = V_{III} - V_I$$

r = radius

$$\pi r^2 = \frac{V_{III} - V_I}{l_D}$$

l_D = length between meniscus in V_D

(4) $$r = \sqrt{\frac{V_{III} - V_I}{\pi l_D}}$$

In Figure 13 b one volume of mercury is in two different positions but these positions are overlapped. The shaded area is the overlapped area.

(5) $$V_{II} = V_{IV}$$

(6) $$V_B = V_{II} - V_A$$

(7) $$V_B = V_{IV} - V_C$$

(8) $$V_{II} - V_A = V_{IV} - V_C, \text{ but } V_{II} = V_{IV}$$

(9) $$V_A = V_C$$

(10) $$r_A{}^2 = r_C{}^2$$

(11) $$\frac{r_A}{r_C} = \frac{l_C}{l_A}$$

Thus the large amount of mercury was run through the capillary in an overlapping fashion. Then the small amount of mercury was put in place of one of the lengths l_A or l_C in V_A or V_C respectively as shown in Figure 13 b. If it was placed approximately in V_A then the radius of V_C was established. This V_C radius was then used in equation (11) with the overlap data. The calibration data are compiled in

Tables I and II. l equals the scale readings from the traveling microscope and l' is equal to the distance from the scratch mark on the capillary; the positive and negative signs merely indicate which side of the mark the l' value exists; r equals the radius, $\pi r^2 l'$ equals the volume for the meniscus to the scratch mark. In Figures 14-17 the values l' vs. $\pi r^2 l$ are plotted. As in the case of the interferometric calibration, the calibration graph also had to be placed on large graph paper in order to obtain enough significant figures.

TABLE I - CALIBRATION DATA

CAPILLARY NO. 1

r^2	πr^2	l	l'=(l-m)	$\pi r^2 l'$
.004290	.013477	4.2193	-0.7687	-0.010362
.004290	.013477	4.9994	+0.0110	+0.0001483
.004307	.013530	5.3979	+0.4099	+0.005546
.004307	.013530	6.1749	+1.1869	+0.016059
.004306	.013527	6.5746	+1.5866	+0.031467
.004306	.013527	7.3527	+2.3647	+0.031994
.004310	.013540	7.7537	+2.7657	+0.037448
.004310	.013540	8.5289	+3.5409	+0.047944
.004353	.013675	8.9212	+3.9332	+0.053806
.004353	.013675	9.6888	+4.7008	+0.064307
.004307	.013530	3.8192	-1.1688	-0.015814
.004307	.013530	3.0443	-1.9437	-0.026298
.004324	.013584	2.6424	-2.3456	-0.031853
.004324	.013584	1.8723	-3.1157	-0.042311
.004312	.013546	1.4737	-3.5151	-0.047630
.004312	.013546	0.6987	-4.2893	-0.058120

TABLE II - CALIBRATION DATA

CAPILLARY NO. 2

r^2	πr^2	l	l'=(l-m)	$\pi r^2 l'$
0.003988	0.012529	4.2982	-0.7814	-0.009790
0.003988	0.012529	5.0529	-0.0267	-0.0003345
0.003998	0.012560	5.4555	+0.3759	+0.004721
0.003998	0.012560	6.2083	+1.1287	+0.014176
0.004008	0.012592	6.6074	+1.5278	+0.019235
0.004008	0.012592	7.3502	+2.2706	+0.028587
0.004020	0.012629	7.7520	+2.6724	+0.033752
0.004020	0.012629	8.5029	+3.4233	+0.043236
0.004044	0.012705	8.9019	+3.8223	+0.048581
0.004044	0.012705	9.6463	+4.5667	+0.058043
0.003984	0.012516	3.8940	-1.1856	-0.014844
0.003984	0.012516	3.1374	-1.9422	-0.024316
0.003956	0.012428	2.7348	-2.3448	-0.029146
0.003956	0.012428	1.9704	-3.1089	-0.038644
0.003975	0.012488	1.5734	-3.5062	-0.043792
0.003975	0.012488	0.8138	-4.2658	-0.053280

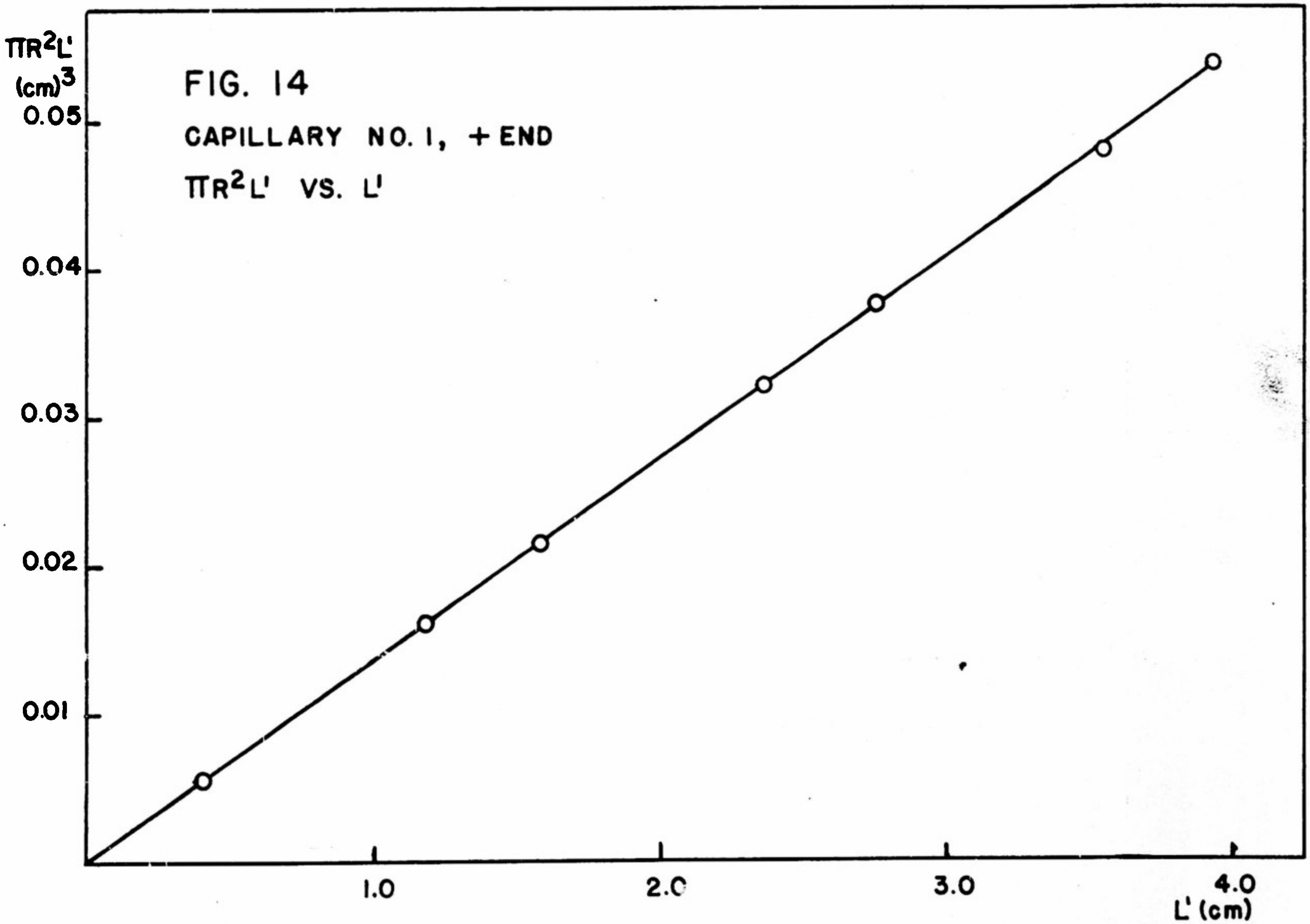


FIG. 14
CAPILLARY NO. 1, + END
$\pi R^2 L'$ VS. L'

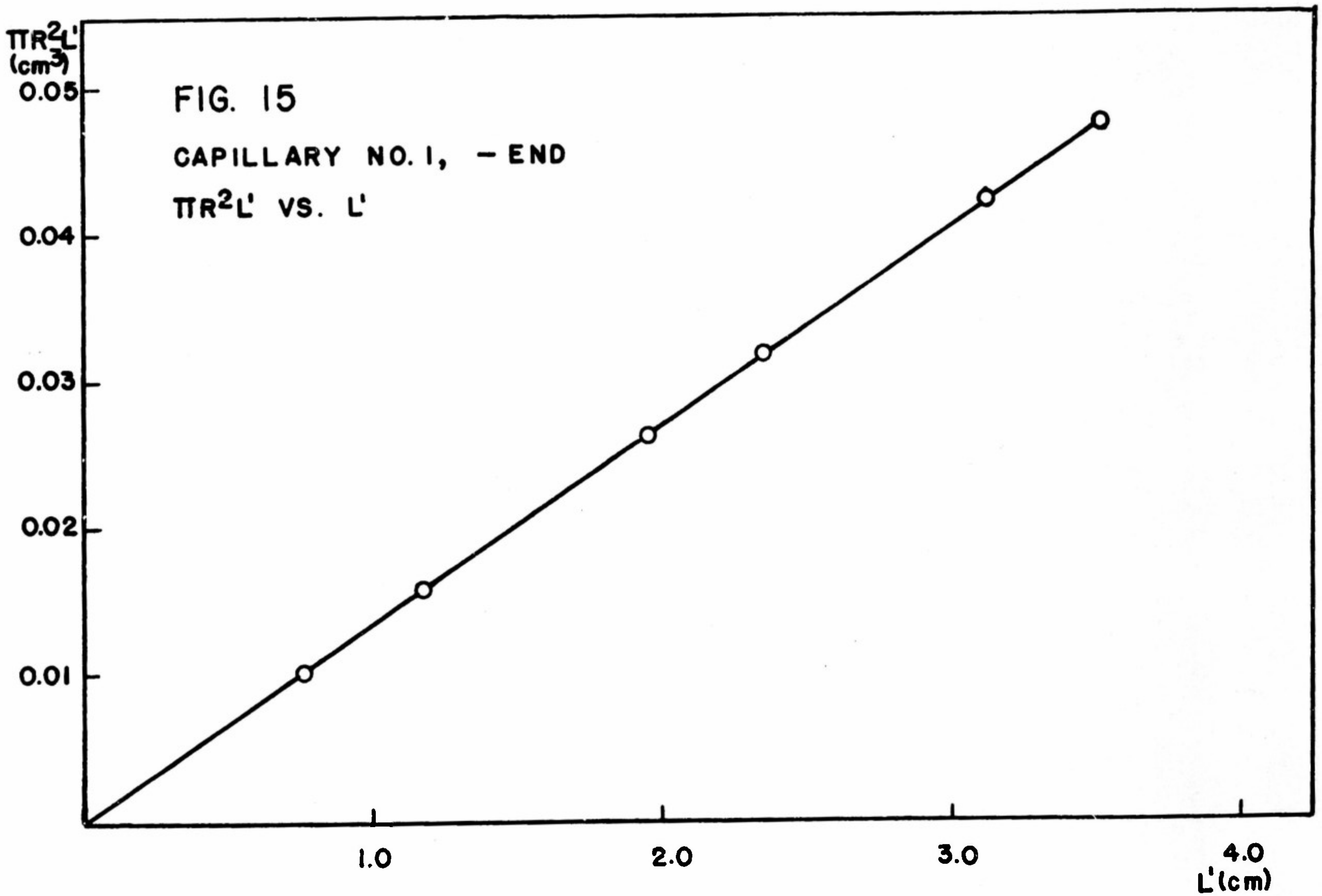


FIG. 15

CAPILLARY NO. 1, – END

$\pi R^2 L'$ VS. L'

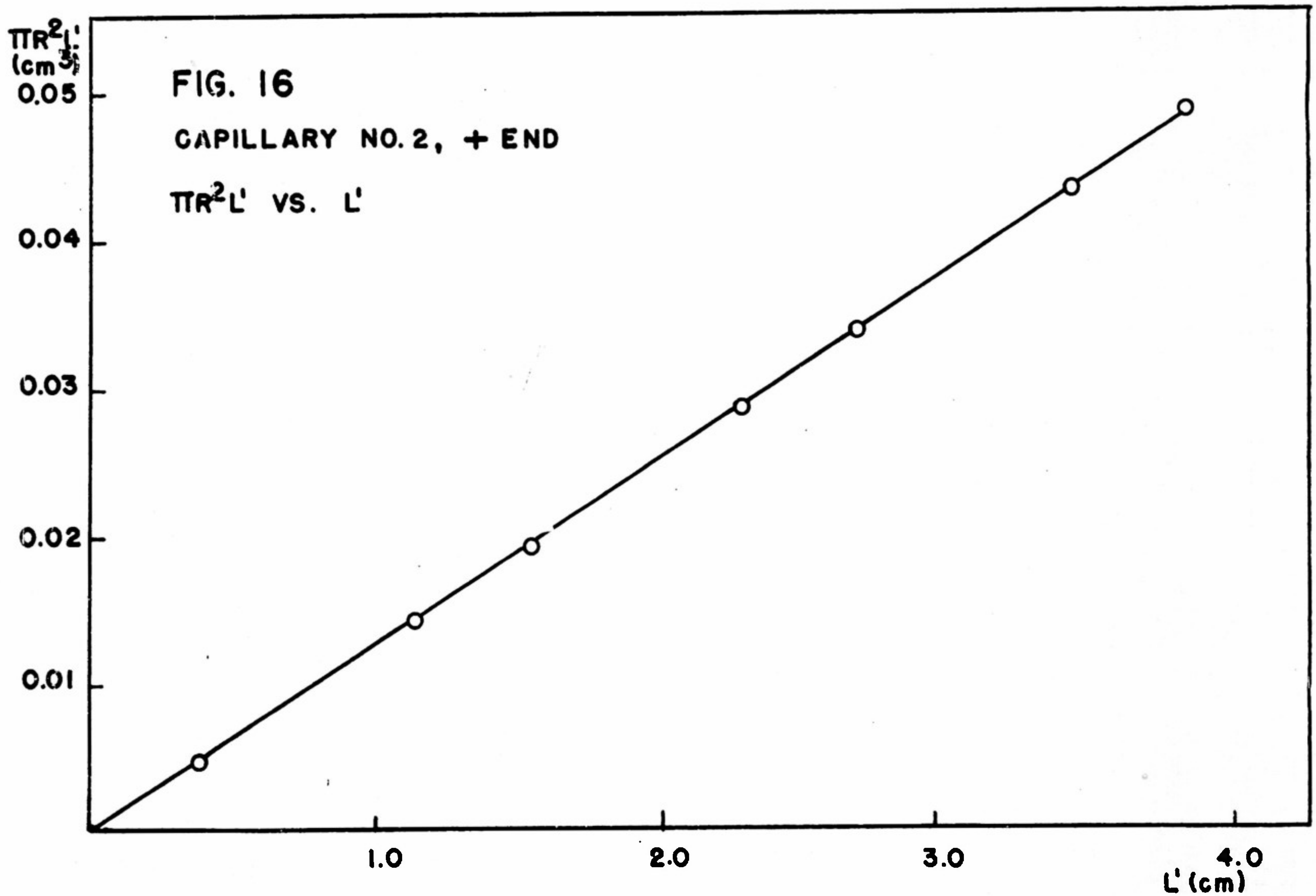


FIG. 16
CAPILLARY NO. 2, + END
$\pi R^2 L'$ VS. L'

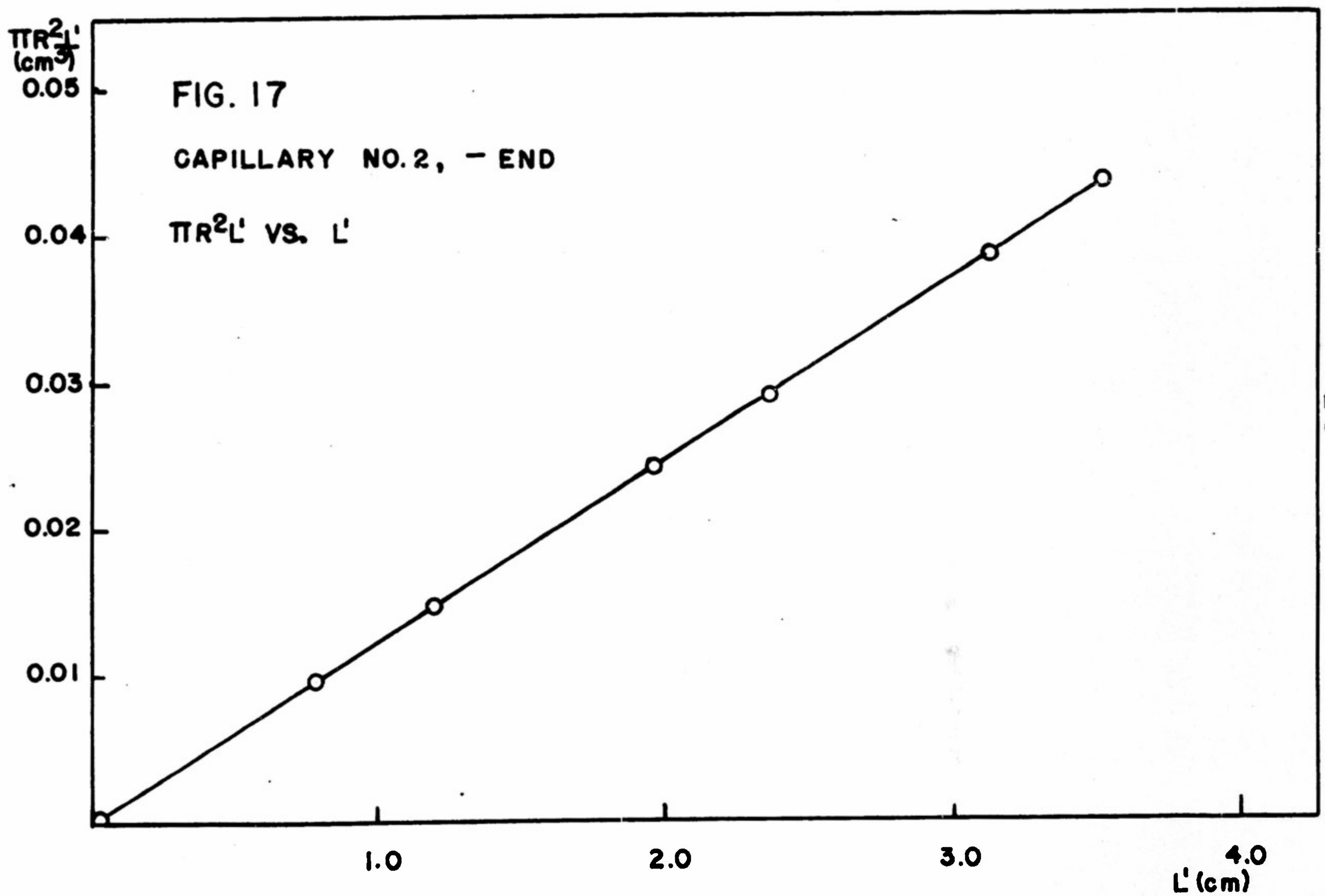


FIG. 17

CAPILLARY NO. 2, – END

$\pi R^2 L'$ VS. L'

2. The Pycnometers and Other Related Equipment

Having calibrated the capillaries they were incorporated into a pair of pycnometers which were built as closely equal in volume and weight as possible. Two pycnometers patterned after the design in Figure 18 were made. Two holes were drilled into a piece of brass stock so that the pycnometers would fit snugly and would not shake due to the motion of water in the bath. This arrangement is shown in Figure 19. The holder was set on a stand in the constant temperature bath at a height so that the water came up to the weighing hooks of the pycnometers. The brass provided a shield from any sudden temperature changes and guaranteed the exact same temperature in each pycnometer. It transmitted heat quickly enough to allow the pycnometers to come to thermal equilibrium in a matter of 20 minutes after placing them in the bath. Although the bath was capable of higher precision with an electronic relay system, density measurements were made at $25.000 \pm .003^{\circ}C$. A Beckman thermometer was used to keep a check on the relative temperature changes. The density measurements were better than those that could have been made with a single pycnometer at $25.000 \pm .001^{\circ}C$.

The volumes or the heights of the liquids in the capillaries were measured by a traveling microscope which is capable, with the proper lens, of measuring height differences of 1×10^{-4}. For this work a lens with a focal length of about 20-30 cm. was used, which gave an accuracy of

FIG. 18

PYCNOMETER DESIGN

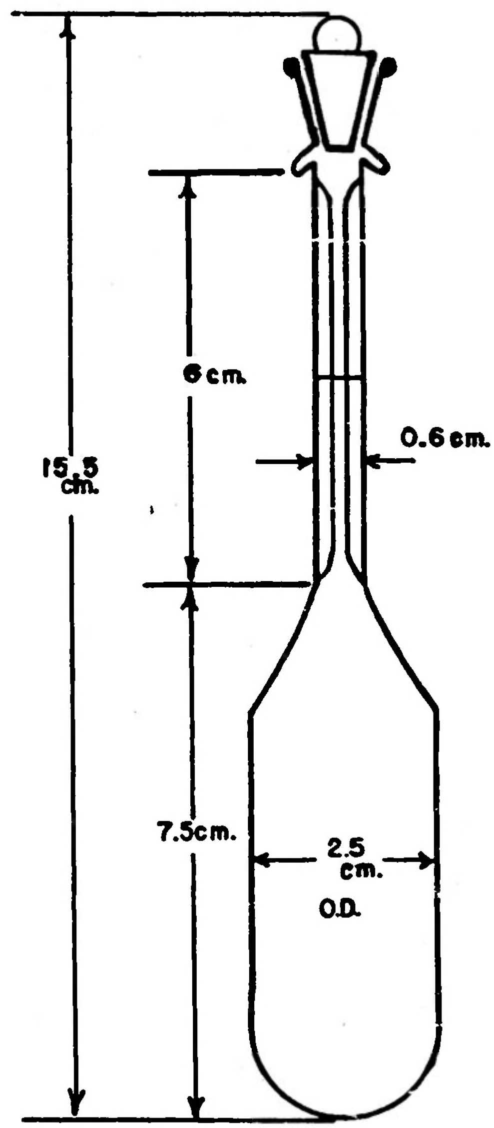
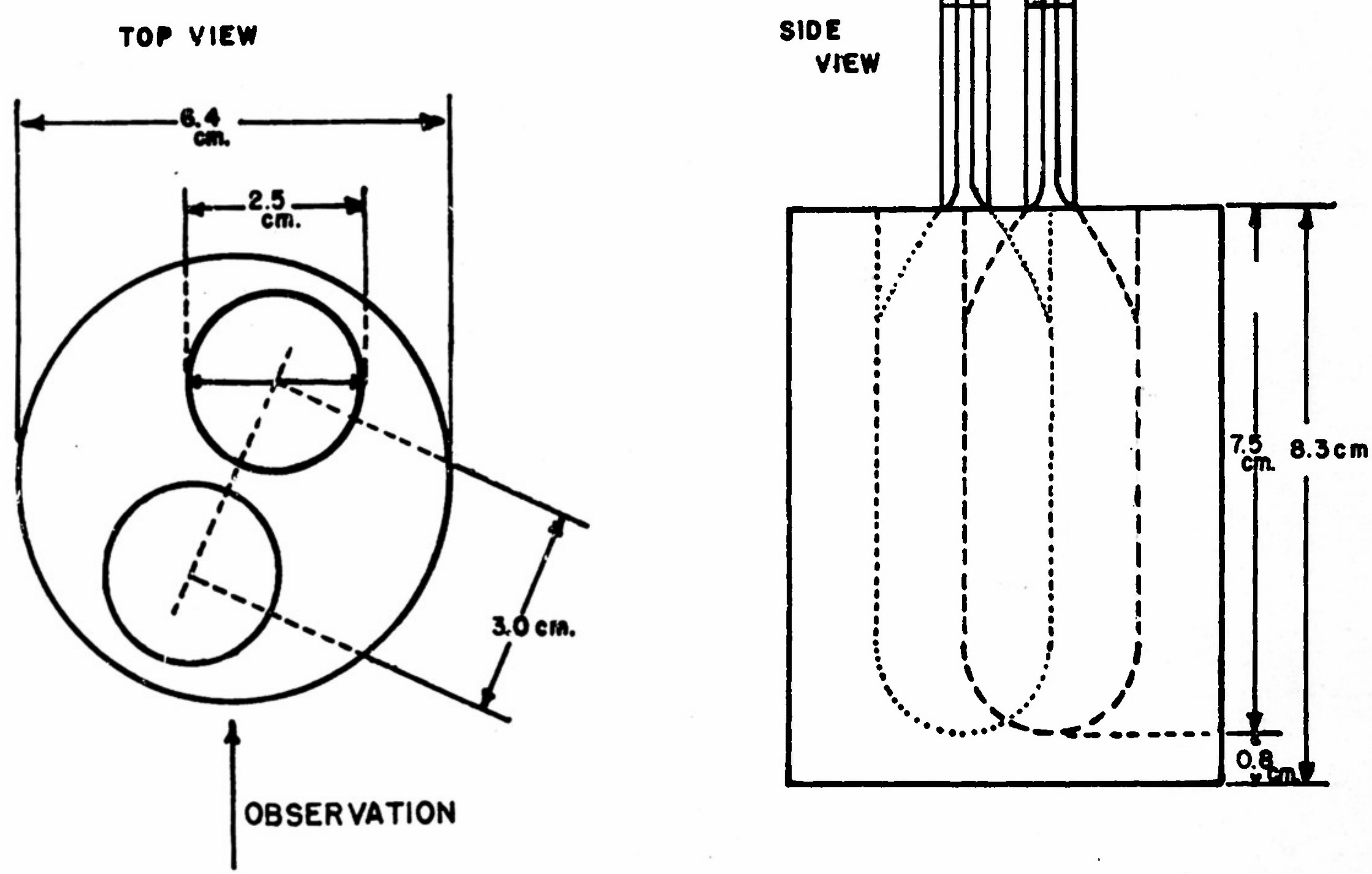


FIG. 19

PYCNOMETER HOLDER



$\pm$ 5 x 10^{-4} cm. The necessity for this type of lens was that in order to observe both capillaries at the same time, the block containing them was rotated from the normal side by side position of the pycnometers to a position where the pycnometers were staggered with one behind the other. See Figure 19. Thus, a lens with a good depth of field was needed. Using the focusing length adjustment for the telescope led to unreproducible results. Once, both pycnometer capillaries were well within the field and both well defined, the telescope was not moved again except to move it in the vertical direction necessary to make the readings.

The balance used for the weighing of the pycnometers was an Ainsworth semi-micro balance. It was used with a 10 mg. rider and the last two figures were determined by the swing method. The sensitivity during this work with a 40 g. load was .013 mg./division. The weights were calibrated against two different 10 g. standard weights. The pycnometers were suspended by their hooks with a Ni-Chrome wire hanger. The pycnometers were weighed without the use of a tare since the subtraction of the pycnometer weights canceled out most of the buoyancy corrections.

Before weighing the pycnometers they were always wiped off in an identical manner, first with a lintless cloth, then with a chamois. They were then allowed to come to equilibrium with the water vapor in the air for 15 minutes. They were weighed once on each pan so that the four weighings were necessary. This weighing procedure took approximately one hour to complete.

3. The Determination of the Pycnometer Volumes

Water was prepared for the calibration by distilling it three times: once with no additive, once with KOH and $KMnO_4$ and lastly with a few drops of H_2SO_4.[1] This water at 25.00°C had a density of 0.997048 g/cc.

Since the calibration of pycnometers is one of the most important experiments it was carried out, assuming nothing about the buoyancy and other correction factors. Also since the experimental detail is similar to that of a regular experiment, which is to follow, a table will merely be used with no explanation to show the procedure of how the volumes and weights were obtained.

Two volumes were determined for each pycnometer, utilizing the upper and lower parts of the meniscus. This is necessary because the concentrated latices are opaque to light and the bottom of their menisci cannot be observed. This does not matter however, since in any one experiment both pycnometers are observed the same way and any correction factor added for using the upper part of the meniscus would cancel out in the subtraction of the two pycnometric volumes to give ΔV.

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[1] A. Weisberger, "Physcial Methods of Organic Chemistry," Vol. I, Part I, Interscience Publishers, 1949, p. 255.

See Table III for all the data pertaining to the determination of V_1 and V_2, where V_1 and V_2 are the volumes of pycnometer one and two, respectively.

In Table III:

P_o = full pycnometer, observed weight

D = density

$$K = \frac{P_o}{D_{brass}} - \frac{P_o'}{D_{glass}} - \frac{P_o - P_o'}{D_{H_2O}}$$

P_o' = empty pycnometer, observed weight

C_4 = correction factor for vapor in capillary

$$K' = \frac{P_o}{D_{brass}} - \frac{P_o'}{D_{glass}}$$

P_c = pycnometer full, corrected weight

P_c' = pycnometer empty, corrected weight

ΔP_c = weight of water

Δh_1 = distance from lower part of meniscus from scratch mark

Δh_2 = distance from upper part of meniscus from scratch mark

Capill. volume M_1 = volume between lower part of meniscus and mark

Capill. volume M_2 = volume between upper part of meniscus and mark.

TABLE III - PYCNOMETER CALIBRATION DATA

Pycn.→	No. 1	No. 2	No. 1'	No. 2'
P_o	42.68658 g.	42.85320 g.	42.67080 g.	42.83365 g.
P_o/D_{brass}	5.124	5.144	5.123	5.142
$P\delta/D_{glass}$	8.215	9.329	8.215	9.329
$\frac{(P_o-P\delta)}{D_{H_2O}}$	19.214 at 26.9°C	19.602 at 26.9°C	19.199 at 27.4°C	19.580 at 27.4°C
K	22.308	23.787	22.291	23.767
D_{air}	.001109	.001109	.001135	.001135
K x D_{air}	+.02474	+.02636	+.02530	+.02698
C_{vapor}	.00000	.00000	.00001	.00001
P'_c	23.53861 g.	23.32150 g.	23.5386 g.	23.32150 g.
$P\delta/D_{brass}$	2.826	2.780	2.826	2.780
$P\delta/D_{glass}$	8.215	9.329	8.215	9.329
K'	5.389	6.549	5.389	6.549
D_{air}	.001130	.001130	.001130	.001130
K' x D_{air}	+.00609	+.00740	+.00609	+.00740
P_c	42.71132 g.	42.87958 g.	42.69611 g.	42.86064 g.
P'_c	23.54470 g.	23.32890 g.	23.54470 g.	23.32890 g.
ΔP_c (H_2O)	19.16662 g.	19.55068 g.	19.15141 g.	19.53174 g.
D_{H_2O} at 25.00°C	0.997048	0.997048	0.997048	0.997048
Vol. of H_2O	19.22336cc	19.60856cc	19.20811cc	19.58956cc
Δh_1	-0.4303cm	-0.2975cm	+ .7031cm	+1.1290cm
Δh_2	-0.4641cm	-0.3309cm	+ .6770cm	+1.1050cm
Capill. Volume M_1	-0.00538cc	-0.00404cc	+ .00877cc	+0.01532cc
" M_2	-0.00582cc	-0.00448cc	+ .00843cc	+0.01500cc
Pycn. vol.M_1	19.21798cc	19.60452cc	19.21688cc	19.60488cc
Pycn. vol.M_2	19.21754cc	19.60408cc	19.21654cc	19.60456cc
Ave M_1	19.21743cc	19.60470cc		
M_2	19.21704cc	19.60430cc		

4. Procedure and Results

The sequence of steps in a density determination is as follows:

1. Clean and dry pycnometers
2. Weigh empty pycnometers
3. Either filter or centrifuge latex sample
4. Place water in one pycnometer and latex in the other pycnometer
5. Put pycnometers in constant temperature bath and measure volume
6. Weigh full pycnometers
7. Determine concentration of latex
8. Determine ratio between solid latex and water-soluble material
9. Centrifuge latex sample for serum and repeat 1-7 for serum
10. Calculate density.

1. The pycnometers were cleaned by squirting the inside with soapy lukewarm water or organic solvents, if needed. They are then rinsed with distilled water and reagent grade acetone and placed in a vacuum desiccator. The desiccator was completely evacuated three times and clean dust-free air allowed back in.

2. The buoyancy corrections canceled out for the empty pycnometers but for weighing full ones the necessary data

must be collected for the calculation of the air density: barometric pressure, temperature and the per cent humidity. The pycnometers were weighed once on each pan. They were wiped with a lintless cloth and then a chamois-skin and allowed to come to equilibrium before each weighing. The tops had to be loosened just before weighing.

3. After the measurements were made the latex sample was prepared either by centrifuging (the usual method), or in the case of a particularly coagulated one, filtered through a pyrex sintered glass filter with the aid of a water pump.

4. The sample was then placed in the pycnometer by means of a syringe needle fitted to the end of a 25 ml. pipette. Pressure was applied to the top of the pipette by the use of a rubber bulb. After the addition of the sample, a preliminary cleaning of the neck and capillary were made. At this point the sample was placed in the constant temperature bath for a half-hour to see if any air bubbles were going to form. If no air bubbles formed, the cleaning of the pycnometer was finished. Wire with lens tissue wrapped around was used like a pipe cleaner for this purpose. If an air bubble did form then it had to be removed with a syringe and needle after it had risen into the capillary. After the capillary and the neck of the pycnometer had been cleaned, the pycnometer, along with the other one which had been filled with the specially prepared water, were put into the bath until equilibrium was reached.

5. Using the traveling microscope, the heights of the liquids in the capillaries was determined after loosening the tops and making sure that the temperature is in the right range.

6. The pycnometers were then weighed in a procedure similar to that used for the empty pycnometers.

7. The latex concentration is easily determined on two 10 cc. samples placed in weighing bottles weighed and placed in the drying tower which is under a partial vacuum and heated by boiling alcohol. After drying, the sample was reweighed and the concentration was expressed as g/100 g of latex.

8. The ratio, expressed as K, of the water-soluble material was determined by centrifuging out the solid polymer and decanting or pipetting out the supernatant liquid. Sometimes, freezing had to be employed prior to centrifuging in order to effect a separation of polymer and serum. The solid polymer was washed and centrifuged a second time. Once more the supernatant liquid was removed and the entire cycle repeated. By a simple calculation it was shown that weighable amounts of water-soluble material can be removed in two washings. Then both components were placed in the drying tower, mentioned previously.

The dry residues were weighed and the ratio, K, establlished.

9. Finally, the density of the water-soluble material

was determined using 25 ml. of serum.

10. The experimental data were then inserted into equation II-15 in order to obtain the apparent density of the polymer.

The density of the polymer was determined for nine different particle sizes, five for polystyrene and four polyvinyl toluene. No apparent effects of particle size on density was found. Table IV gives the complete data for both polymers.

TABLE IV - DENSITY RESULTS

a. Polystyrene

Dia (mμ)	c_1	d_{12}	K	d_3	d_2
240	.59535	1.02318	.007842	2.62	1.0593
280	.55769	1.02480	.005121	3.07	1.0587
300	.61442	1.02016	.005339	4.74	1.0546
540	.67425	1.01685	.006960	2.78	1.0559
950	.75856	1.01143	.00683	2.24	1.0556

Ave 1.0569 $\pm$ .0019

b. Polyvinyl Toluene

58	.74054	1.00989	.009894	4.91	1.0243
373	.54691	1.01323	.008348	3.28	1.0276
590	.68535	1.00692	.00555	2.569	1.0255
935	.965980	1.00108	.1984	2.052	(1.0386)

Ave 1.0258 $\pm$ .0012

CHAPTER III

REFRACTIVE INDICES

A. <u>The Literature Survey</u>

Very little data can be found on the refractive index of latices. Values for the solid polystyrene and polyvinyl toluene, however, are reported as: n_D 20°C = 1.5920 for polystyrene, n_D 20°C = 1.5831 and 1.5766 for poly meta vinyl toluene and poly para vinyl toluene, respectively.[1]

Recently a research group in Germany used the refractive index of polystyrene latex as a measure of its coagulation by methyl cellulose.[2] They agitated their samples just before each refractive index measurement was made and found a decrease in refractive index which could not be accounted for by the refractive index of the added methyl cellulose. This leads to the assumption that the coagulated or larger size particles did not contribute as much to the total refractive index as the uncoagulated particles did. These investigators also found that in the use of the so-called Beer-Landolt mixture rule, an increase in concentration leads to

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[1]R. H. Boundy and R. F. Boyer "Styrene," New York: Reinhold Publishers Corp., 1952, p. 1239.

[2]O. Diele, H. Krämer and W. Klause, <u>Kolloid Zeit.</u>, <u>130</u>, 105-10 (1952).

a decrease in apparent refractive index of the suspended particle. The concentration range they checked was from one to four per cent. Their value was approximately 1.60. The decrease in the fourth decimal place was systematic but was two places removed from a significant figure. This decrease, however, is in accordance with the theory on the use of this equation.[1] This Beer-Landolt mixture rule is also the one used in this investigation, and it is described later.

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[1]W. Heller, Phys. Rev., 68, Nos. 1 and 2, 5 (1945).

B. Theoretical

In order to determine the refractive index of latex, a model A Rayleigh interferometer[1] was used which allows the precise measurement of small changes in the refractive index of liquids and gases without the necessity of stringent temperature controls. The $\Delta n/\Delta t$-values where Δn is refractive index difference and Δt is temperature change, shows little change for solid material and one can operate over a temperature range of $\pm 3^{\circ}C$ without any effects to the final result, providing there is no temperature difference between the cells containing the medium and the latex during measurements. A further description of the operation of the instrument and the method of collection of data will be reserved for Part C.

From the interferometer, Δn or $(n_{12}-n_1)$ is obtained to a precision of $\pm .000001$ where n_{12} and n_1 are the refractive indices of the solution and the medium, respectively. Thus, taking the known refractive index of the medium and adding Δn, one obtains n_{12}. According to the empirical mixture equation known as the Beer-Landolt equation:[2]

$$n_{12} = n_1\phi_1 + n_2\phi_2 \qquad (1)$$

where n_2 is the refractive index of the polymer and ϕ_1 and ϕ_2 are the volume fractions of the medium and the polymer,

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[1] Baird Associates, Inc., Cambridge, Massachusetts.

[2] W. Heller, loc. cit.

respectively.

In order to obtain a refractive index of the polymer to four figures with the error in the fourth, a concentration had to be determined which would satisfy this requirement: Equation (1) is transformed to yield:

(2) $$n_2\phi_2 = n_{12}-n_1\phi_1$$

and if $\phi_1 \cong 1$, then $n_{12}-n_1$ must at least equal .001000 to obtain the four required figures

(3) $$n_2\phi_2 = .001000$$

and using $n_2 \cong 1.6$

(4) $$\phi_2 \cong .000625 \frac{\text{c.c.}}{\text{c.c.}}$$

This concentration of latex which is approximately .063% cannot be checked in the interferometer due to the light scattering of latex. The scattering makes the fringes in the optical field so indistinct that for a particle of 200-300 mμ in diameter, one can only check concentrations up to a maximum of .010%. For large particles, 500-900 mμ concentrations higher than .004% produced these indistinct fringes. However it was found that the drum readings which are proportional to Δn values could be read more accurately than to 10^{-6}. By plotting these values against concentration and calculating the slope by the least mean square method, a slope was determined which could be used to calculate Δn for concentrations ten-fold higher and still have the error in the fourth figure (or sixth decimal place). Thus n_2 could be determined to the required four figures.

The volume fractions ϕ_2 and ϕ_1 were easily determined through the weight fractions and the densities of the polymer and latex. Since $\phi_2 + \phi_1 = 1$, then only **one** ϕ had to be determined. Thus, one may convert from the weight fraction to the volume fraction in the following manner:

$$(5) \qquad c_2 = \frac{w_2}{w_2 + w_1}$$

where c_2 = weight fraction of polymer

w_2 and w_1 = weights of polymer and solvent, respectively, in a latex sample.

$$(6) \qquad \phi_2 = \frac{d_{12}}{d_2}$$

where d_1 and d_{12} = the densities of the polymer and the latex, respectively.

$$(7) \qquad \text{or } \phi_2 = c_2 \frac{\theta_2}{\theta_{12}}$$

where θ is the specific volume or the inverse of the respective densities.

The density of the solution d_{12} is obtained from the mixture rule which was used in Chapter II, B. This rule is needed now to show the complete determination of ϕ_2:

IIB-7

$$\frac{1}{d_{12}} = \theta_{12} = \theta_1 c_1 + \theta_2 c_2$$

$$\therefore (8) \qquad \phi_2 = \frac{c_2\theta_2}{c_1\theta_1 + c_2\theta_2}$$

Converting to densities:

(9) $$\phi_2 = \frac{\frac{c_2}{d_2}}{\frac{c_1}{d_1} + \frac{c_2}{d_2}}$$

(10) $$\phi_2 = \frac{c_2 d_1}{c_1 d_2 + c_2 d_1}$$

and since $c_1 = 1-c_2$

(11) $$\phi_2 = \frac{d_1}{d_1-d_2 + \frac{d_2}{c_2}}$$

and similarly for ϕ_1:

(12) $$\phi_1 = \frac{d_2}{d_2-d_1 + \frac{d_1}{c_1}}$$

The effect of impurities and stabilizers to the refractive index of the latex was investigated after it was found that they had a profound effect on the density. The densities however were determined with 25-40% latices while the n_2 values were determined at .001 to .007%. The effect, was checked first by calculation and then by experiment. The water-soluble material was found to be phosphate and assumed to be complex phosphate. The calculations were as follows:

(13) $$n_{13} = n_1\phi_1 + n_3\phi_3$$

(14) $$\Delta n = n_1(\phi_1 - 1) + n_3\phi_3$$

where n_3 and ϕ_3 are the n and ϕ of the water soluble impurities; n_{13} = total refractive index (with no latex) substituting $1-\phi_3 = \phi_1$

$$1 \times 10^{-6} = n_1(1-\phi_3-1) + n_3\phi_3$$

$$1 \times 10^{-6} = (n_3-n_1)\phi_3$$

and since $n_1 = 1.33$ and $n_3 = 1.45$ = refractive index of complex phosphate

$$\phi_2 = \frac{1 \times 10^{-6}}{.12} = 8 \times 10^{-6}$$

This means then that 8 parts per million of impurities by volume (or approximately by weight) could be detected by the interferometer.

Then using a latex sample which contained 24% polymer solids and 0.3% water soluble materials, calculations were made to follow the per cent polymer and particularly the per cent water soluble material in the interferometric sample. This ratio of 24% to 0.3% was the lowest ratio used in this investigation. Higher ratios, of course would be even less detectable than the lower ones.

TABLE V - H_2O-SOLUBLE MATERIAL CONCENTRATION

Original latex concentration	24 g/100 g
Original max. H_2O soluble material concn	.3 g/100 g
Max. latex used in n determination .	.008 g/100 g
Corresponding H_2O soluble material concn.	1.0×10^{-4} g/100 g
Latex wt. fraction (approx. ϕ_2). .	.00008
H_2O-soluble material wt. fraction (approx. ϕ_3).	1.00×10^{-6}

After looking at Table V and comparing the result with the detectable amount, 8×10^{-6}, one can see that there is approximately a ten-fold "safety factor." But, to be sure of this, an experiment was carried out. First a concentration of latex (.006%) was checked after centrifuging the sample to remove all the latex. The results showed no detectable difference in refractive index between water and the centrifuged sample. Then, in order to find just what the magnitude of the Δn was at the lower concentrations, a 1% latex sample was centrifuged and the serum refractive index determined. The drum reading difference which is proportional to Δn and called ΔR had a value of 18.3. These ΔR values under good conditions are reproducible to $\pm$ 0.5. The reading difference was plotted against concentration of latex and extrapolated back to zero. See Figure 20. The ΔR value of a 0.008% latex after centrifuging would be 0.15 units which obviously would be too small to detect.

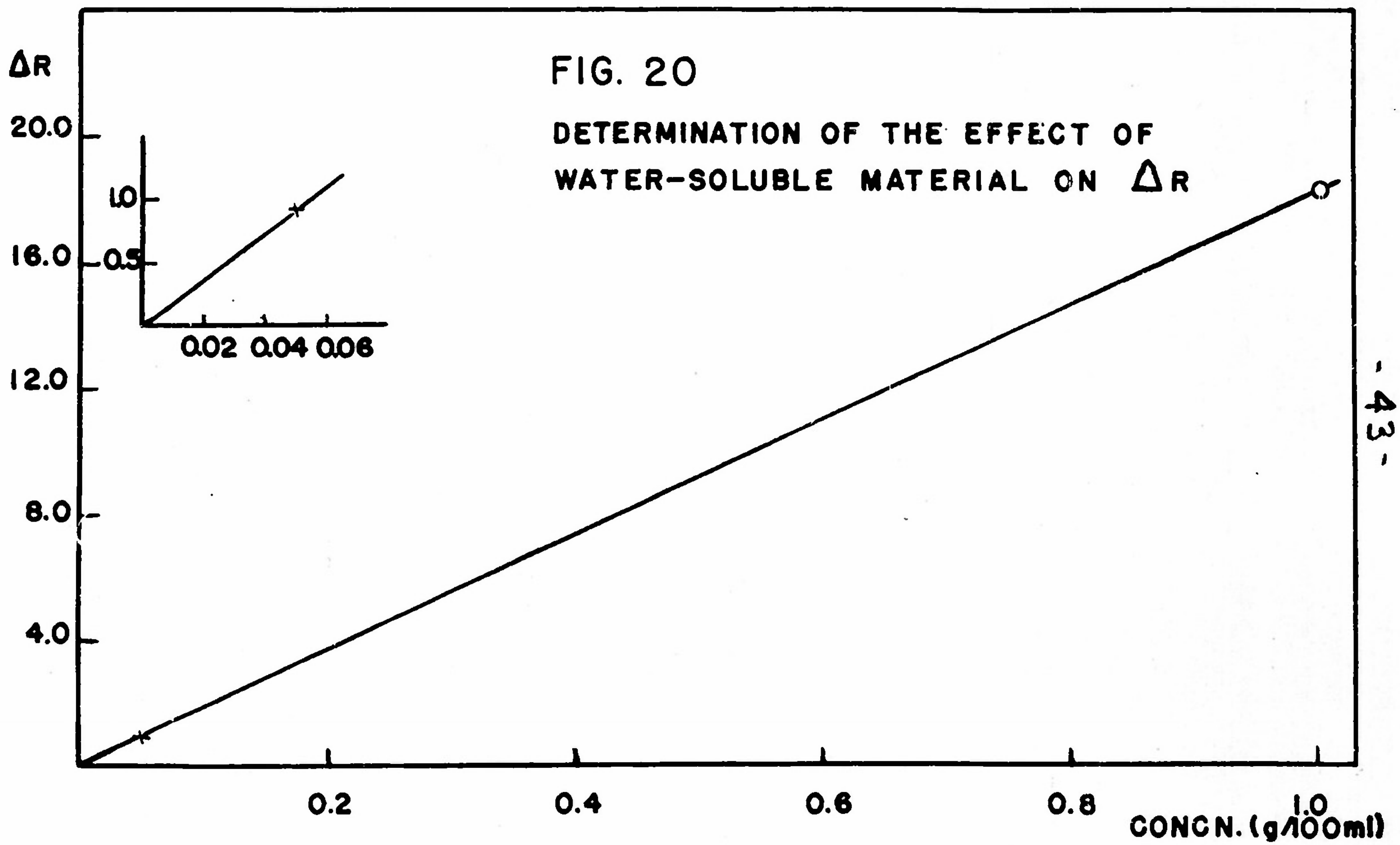


FIG. 20

DETERMINATION OF THE EFFECT OF WATER-SOLUBLE MATERIAL ON ΔR

C. Experimental

1. The Interferometer

The Rayleigh interferometer is capable of measuring refractive index differences of liquids in a one cm. cell to a precision of 1×10^{-6}. The cell consists of two compartments, side by side, of which one was used for latex and the other for pure double-distilled water. At the start and the end of one series of measurements (usually five or six samples) the zero point was checked. This zero point is checked by placing pure water in both cell compartments.

Before any experiments are run with the instrument a check of the linearity of scale with fringe displacement had to be made. This check was made with the cell with H_2O in both sides to eliminate any errors in the calibration graph due to defects in the cell. Since the wave length of the light is known (546.1 mu) by using a proper filter, the distance between the fringes is known. Thus the distance can be plotted against ΔR. ΔR is the difference between the zero point or zero fringe order and the fringe of the i th order, f_i. A reduced picture of the resultant calibration graph may be seen in Figure 21 produced from the data in Table VI. In order to obtain enough figures, the graph used in the laboratory was plotted on a 30 cm. by 40 cm. graph. Two different one cm. cells were used during this investigation and both were calibrated. If the distance from the zero fringe order to f_1 is divided by the length of the cell (1 cm.) Δn values can be plotted directly.

TABLE VI - INTERFEROMETER CALIBRATION DATA

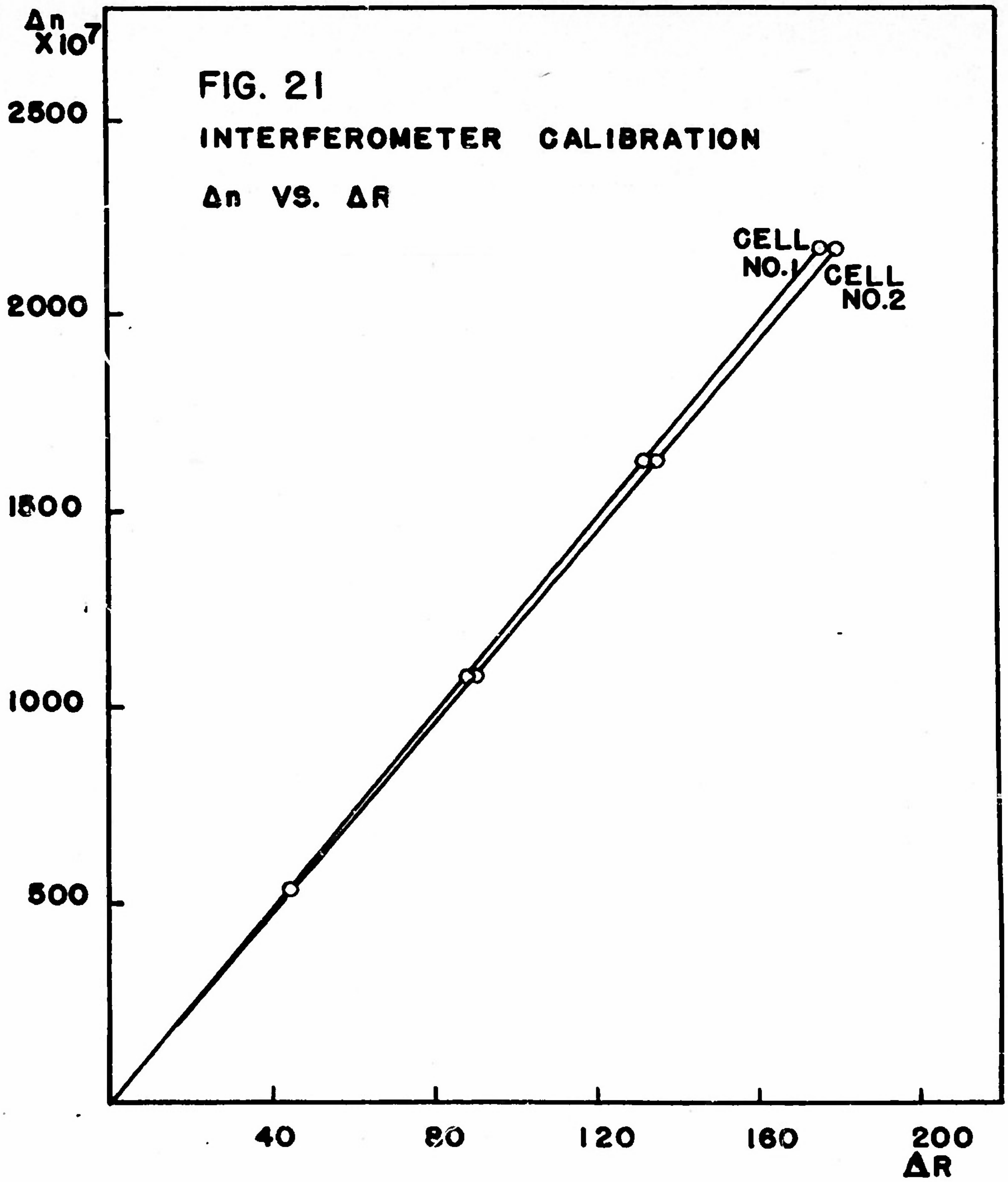
f_1	R_1	ΔR_1	$\Delta n \times 10^8$	R_2	ΔR_2
0	534.0	0		473.5	0
1	578.3	43.8	5461	518.9	45.4
2	623.0	88.5	10920	564.8	91.3
3	667.1	132.6	16380	609.3	135.8
4	711.0	176.5	21840	653.1	179.6
5	755.1	220.6	27310	697.2	223.7
6	-	-	32770	740.9	267.4

(Subscript numbers refer to respective pair of cells.)

2. The Latex Samples and the Procedure

When a latex sample was checked, five to seven dilutions were made from a stock solution. This arrangement had to be used because the low concentration needed for determinations were of no use for gravimetric determinations.

The concentration determination was expressed as g/100 g of latex. However, the stock solution was now diluted by volume to a tenth of its original concentration and was called the secondary-stock solution. This secondary-stock solution was again diluted, thus leading to two errors, the importance of which are checked as follows: The original


Δn
X10⁷
FIG. 21
INTERFEROMETER CALIBRATION
Δn VS. ΔR
2500
2000
1500
1000
500
CELL
NO.1
CELL
NO.2
40
80
120
160
200
ΔR

stock solution concentration was 0.7931 g./100 g. of latex. To make volume dilution without errors the g./100 g. concentration is merely converted to a g./100 ml. concentration by multiplying by its latex density (.99727). 0.7912 g./100 ml. is the result of this converstion. Using this concentration produces the concentration under (B) in Table VII after dilution. The concentrations under (A) are the dilutions assuming that the density of latex is one. After making the volumetric dilutions in (B) in Table VII, the concentrations were converted back to g./100 g. using a latex density of .99705. This conversion to (C) in Table VII is accomplished by dividing (B) by the density of the latex (.99705). As one can see (A) and (C) almost coincide and the error is only 0.05% which is not detectable in the interferometer at these low concentrations.

TABLE VII - DILUTION ERROR DATA

(A)	(B)	(C)
Concn. g./100 g.	Concn. g./100 cc.	Concn. g./100 g.
0.001586	0.001582	0.001587
0.003172	0.003165	0.003174

The ordinary errors in volume measurements are encountered in the possible errors for the glass ware and burettes. Since two dilutions are necessary to obtain the latex concentrations used in the interferometer, the possibility of dilution errors exists. With 100 ml. volumetric flasks of ±.16 ml. accuracy and a 10 ml. burette which has a possible error of ±.02 ml., the most error that can be obtained from two successive one-tenth reductions in concentration using a 0.8 g./100 g. latex as a stock solution is 0.8%. This error however would only occur if all the possible dilution errors were additive. Of course, this very rarely happens and this was shown by lack of scattering of the points on the ΔR versus the concentration graphs.

By using a graph and the least-mean-square method for slope determination, the effect of this error upon the results was reduced considerably. The least-mean-square method gives more weight to higher concentrations where the absolute errors are smaller.

Once the calibration graph and assurances of reproducible concentrations are made, the samples of latices are run in the interferometer to determine the value of Δ n/c. The following procedure was used: 2-4 cc. of a 30% latex were added to 125 ml. of double distilled water in a centrifuge bottle which was spun at 1500 rpm for 30 minutes. One hundred ml. were pipetted into a sterilized, 100-ml. pyrex volumetric flask. The solution, which is the stock solution, was shaken to ensure homogeneity. The secondary-stock solution is prepared by pippetting 10 ml. of stock solution into a second 100-ml. flask and diluted to the 100 ml. mark. At the same time, two 30-ml. samples of the stock solution are placed in weighing bottles, weighed and evaporated to dryness in a drying tower under a partial vacuum and the heat of boiling alcohol. After they were dried and were reweighed, the concentrations were expressed as g./100 g. of latex. In Table VIII is a sample of an experiment carried out to determine the $\Delta R/c$ value. This $\Delta R/c$ value is used later to calculate the ΔR value for an assumed concentration: 0.08000 g./100 g.

TABLE VIII - SAMPLE REFRACTIVE INDEX DETERMINATION

Stock Sub-stock Ml. of Sub-stock	CONCN. 0.6889 0.06889	R	ΔR
0	0.0000000	64.5	0.0
1	0.0006889	65.7	1.2
3	0.0020667	69.0	4.5
5	0.0034445	71.9	7.4
6	0.0041334	73.4	8.9
8	0.0055112	75.8	11.3
10	0.006889	79.0	14.5

The ΔR readings are plotted versus the concentration to check on any points that might be too far from the best straight line. For this plot see Figure 22. In a second table the least mean square equation was calculated and the slope of the line determined from this equation. Since this method is a standard practice it will not be illustrated here. The equation of line in this case was found to be:

$$\Delta R = -0.00_4 + 210_{4.3}c$$

and the slope:

$$\frac{\Delta R}{c} = 210_{4.3}$$

where c = g./100 g. of latex.

Then once the equation is evaluated any c can be used. In the final calculation, a c of 0.08 g./100 g. was used. ΔR was calculated and Δn determined from the calibration graph, Figure 21. Using $n_{12} = \Delta n + n_1$, the n_{12} value is calculated.

3. Results

These average densities of the two polymers were inserted in the refractive index equation, III B, (12), and using equation II B, (1), the refractive indices of the polymers were calculated. These results are given in Tables IX and X. In Figure 23 the particle size versus the apparent refractive index is plotted. It shows a definite decrease in apparent refractive index with increase in particle size. Sixteen different particle sizes of polystyrene and polyvinyl toluene were investigated, employing the average densities from Table IV.

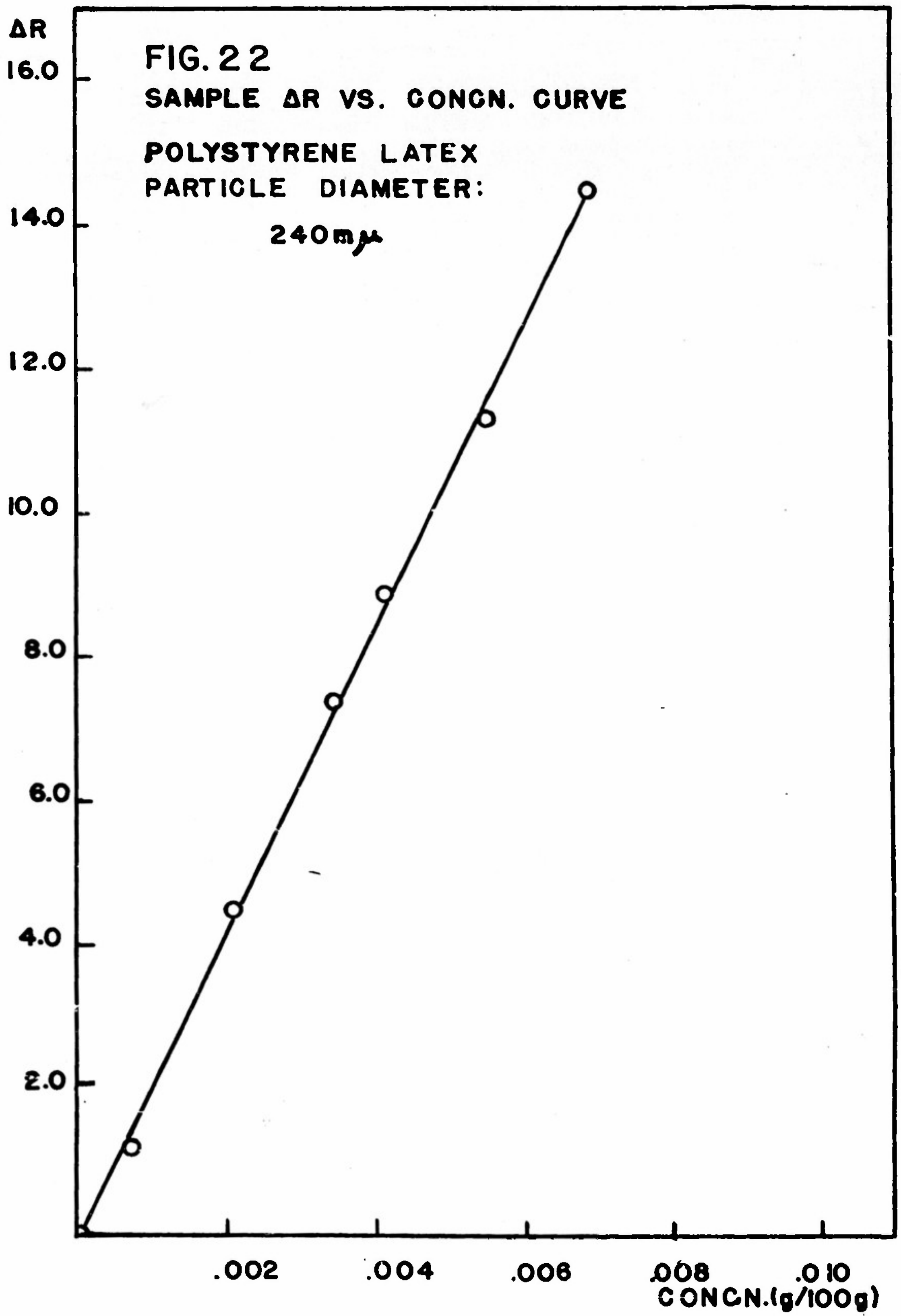

ΔR
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
FIG. 22
SAMPLE ΔR VS. CONCN. CURVE
POLYSTYRENE LATEX
PARTICLE DIAMETER:
240mμ
.002
.004
.006
.008
.010
CONCN.(g/100g)

TABLE IX

REFRACTIVE INDEX vs. PARTICLE SIZE;

POLYSTYRENE

Dia. (mμ)	$n_{546}25^{o}C$
143	1.62_{18}
218-30	1.62_{18}
240	1.60_{98}
252-63	1.60_{85}
256-79	1.60_{59}
280	1.59_{26}
275-99	1.60_{85}
276-314	1.58_{73}
540	1.56_{61}
700-900	1.50_{91}
950	1.49_{85}

TABLE X

REFRACTIVE INDEX vs. PARTICLE SIZE;

POLYVINYL TOLUENE

Dia. (mμ)	$n_{546}25^{o}C$
58	1.59_{72}
177	1.57_{67}
373	1.58_{95}
595	1.55_{61}
770	1.49_{69}

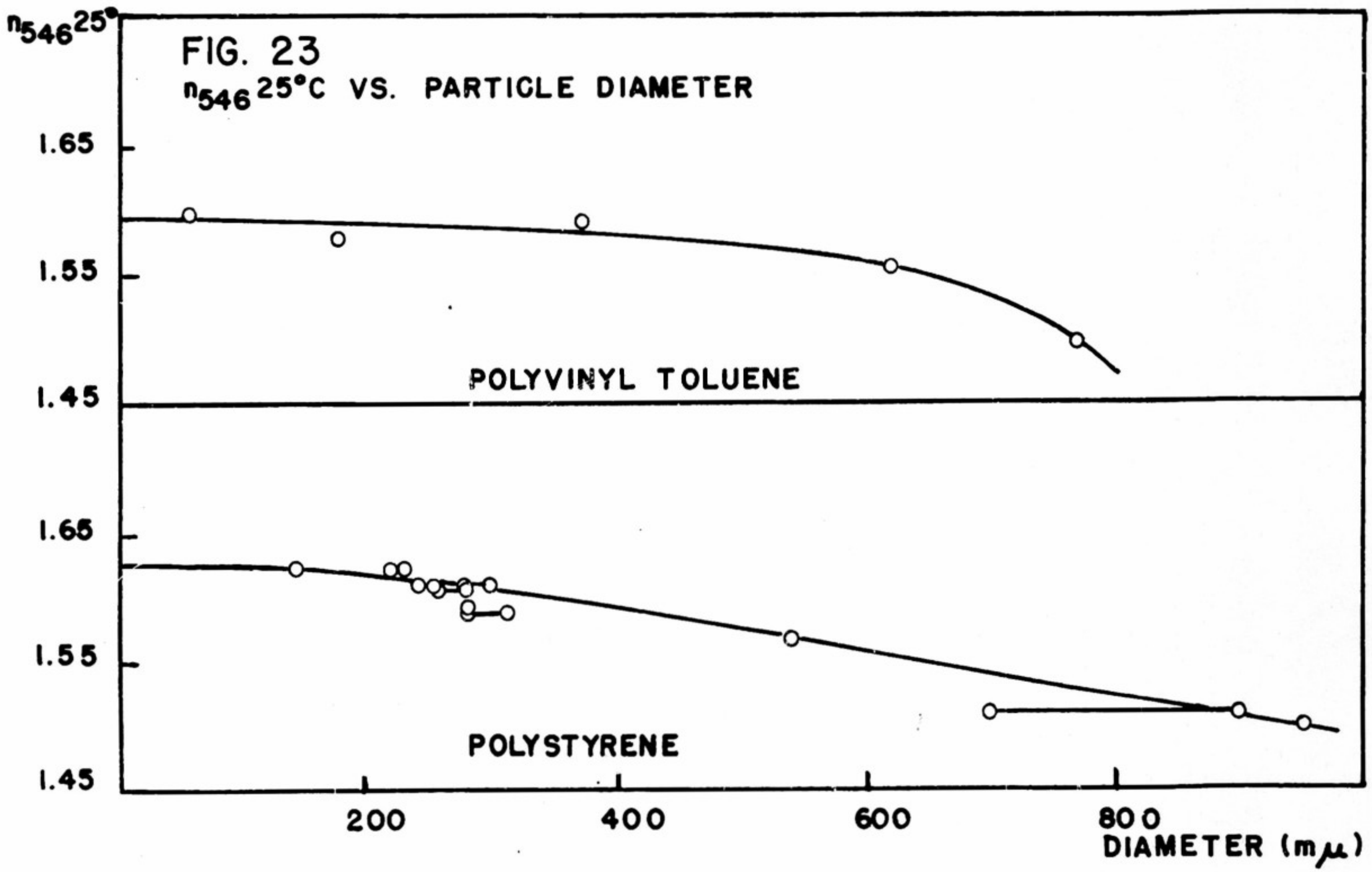


FIG. 23
n_{546} 25°C VS. PARTICLE DIAMETER

CHAPTER IV

DISCUSSION

The decrease of apparent refractive index with increasing particle size is very surprising since constancy in density data is usually accompanied by constant n-values.

It appears, therefore, that the mixture rule given by equation III B, (1) may not be applicable unless the dispersed particles are very small.

In fact, extrapolation of the curves to zero particle size in Figure 23 leads to refractive indices which upon insertion in light scattering equations, bring about very satisfactory agreement between the theoretical work of Mie and the experimental work of Tabibian. These values of n_2 obtained by the extrapolation are 1.595 for polyvinyl toluene and 1.625 for polystyrene.

It is interesting to note that the density of polystyrene is in good agreement with that of Kahler and Lloyd: 1.0569 compared to 1.055, respectively. The only comparison for the polyvinyl toluene is to the solid which has been reported as 1.022 or 1.030 depending on the functional position. This investigation showed a comparative value of 1.0858 which falls midway between the two reported values.

CHAPTER V

SUMMARY

1. A set of differential pycnometers were made for accurate density determinations.

2. The density of the suspended particles of a latex was determined to four significant figures for eight different latex samples.

3. Average densities of polystyrene and polyvinyl toluene were $1.0569 \pm .0019$ and $1.0258 \pm .0012$, respectively.

4. Refractive indices of three significant figures were determined for 16 different latex samples.

5. The refractive indices of polystyrene and polyvinyl toluene polymers decrease as their particle size increases.

6. A similar phenomenon has been noted in a coagulation experiment by another investigator.

7. The phenomenon may be due to a breakdown of the mixture rule at large particle sizes.

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